



# Boundary conditions and heat resistance at the moving solid–liquid interface



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## HIGHLIGHTS

- To obtain conditions at the moving solid–liquid front the model of Gibbs interface is used.
- The temperature discontinuity across the solid–liquid front has been found analytically.
- Effect of Kapitza resistance on the interface kinetics is analyzed analytically.

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## ABSTRACT

Boundary conditions for the solid–liquid interface of the solidifying pure melt have been derived. In the derivation the model of Gibbs interface is used. The boundary conditions include both the state quantities of bulk phases are taken at the interface and the quantities characterizing interfacial surface such as the surface temperature and the surface heat flux. Introduction of the surface temperature as an independent variable allows us to describe the scattering energy at the interface. For the steady-state motion of the planar interface the expression for the temperature discontinuity across the phase boundary has been obtained. Effect of Kapitza resistance on the interface velocity is considered. It is shown that heat resistance leads to non-linearity in solidification kinetics, namely, in “velocity-undercooling” relationship. The conditions of the steady-state motion of the planar interface have been found.

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## 1. Introduction

Solidification of materials from the liquid state and the phenomena occurring at solid–liquid interface are the object of constantly increasing interest both from the point of view of experimental study and development of theoretical models [1–3]. Thermal processes at the phase interface essentially influence crystal growth and ultimately define final structure of solidifying materials. Well known examples are dendritic growth [4] and the heat trapping with the temperature jump at the interface due to absence of local equilibrium both at the interface [5] and the bulk phases [6]. The temperature jump has been first detected at the interface between liquid helium and metallic substrate and it is well known as the Kapitza resistance against heat transport [7].

The existence of heat resistance means that the energy exchange at the interface includes not only the transverse energy transfer but, generally speaking, the energy flux along the interface. This has been namely observed in experiments on water

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droplet evaporation from the warmed Au-substrate [8]. It has been found that a big part of heat energy is transferred parallel to the water–metal boundary through the adsorbed layer, leading to measurable interfacial temperature discontinuity.

Influence of Kapitza resistance on experimental data is a subject of well established discussions within the modern theories and models [9]. Taking into account experimental results [8], Palmieri et al. [10] have supposed that the temperature discontinuity can also be essential at the moving phase interface, especially during fast solidification. These authors have considered influence of Kapitza resistance on the planar front dynamics during of solidification from undercooled state. In their analysis, the kinetic equation for the rate of phase changes has been used that determines in fact the interface temperature for the case of the temperature discontinuity across the interface. For the system where all material constants are identical within both phases the interface temperature was introduced as a half-sum of boundary temperatures of the each phase.

In the linear approximation with respect to an equilibrium boundary conditions at the interface were obtained in Ref. [10] and present the set of Onsager relations [11]. In these relations, the dissipative currents are the solidification rate and the energy flux through the interface and driving forces are interphase temperature jump and departure of the interfacial temperature from the equilibrium temperature  $T_M$  of solidification. It should be noted that the notion about the interfacial boundary conditions as Onsager relations have also been suggested in the work of Brener and Temkin [12] (see also Ref. [13]) although without introduction of the interface temperature as independent variable and with a different choice of thermodynamic fluxes and their conjugated driving forces.

A general formalism of the derivation of boundary conditions at the moving phase surface has been developed by Bedeaux, Albano and Mazur (BAM) [14,15] (see also Ref. [16]). The thermo-hydrodynamical variables for a surface have been introduced in the spirit of Gibbs concept of the dividing surface for which the extensive surface variables are determined as the surface excesses of the corresponding bulk quantities [17].

The BAM-formalism [14,15] was applied by Caroli et al. to the solidification problem [18]. They have derived the boundary conditions at interface for a binary system but neglected by all surface contributions. In particular case of the pure melt and without convection in bulk phases the boundary conditions of Caroli et al. [18] coincide with those ones suggested by Brener and Temkin [12].

In the present work, the general approach based on BAM-formalism [14,15] is applied to the derivation of boundary conditions at the interfacial surface of the solidifying pure liquids taking into account the contributions from surface variables including the heat flux along the surface (longitudinal heat flux). The obtained boundary conditions are then applied to the analysis of heat resistance effect on planar front dynamics in solidification of a stagnant liquid.

The work is organized as follows. In Section 2, the variables characterizing the interface are introduced and the expression for surface entropy production, obtained in Appendix A, is given. Section 3 is devoted to the derivation of the boundary conditions which then applied to the steady state motion of the interface in Section 4. In Section 5, the temperature jump through the interface is calculated and various regimes of the flat front motion are analyzed depending on the thermal Kapitza resistance coefficient. Conclusion and discussion of the main results are given in Section 6. In Appendix A, the BAM-method is summarized in the context of solidifying pure liquid. Finally, in Appendix B, the modified kinetic equation for the rate of phase change derived in the framework of the Gibbs model of an interface.

## 2. Surface variables and entropy production

At equilibrium, the Gibbs's capillary model considers interface as a surface of a zero thickness (i.e., a sharp interface) separating phases and which is situated within the diffuse zone. The surface is characterized by finite densities of extensive thermodynamic quantities are defined as surface excess densities of bulk state quantities [17]. To describe non-equilibrium states at the moving interface, the surface densities of dissipative fluxes have also been introduced [14,16]. According to BAM-formalism [14], if  $x$  is the density per unit volume of some extensive state quantity (mass density, velocity, energy fluxes and so on), then at any space–time point  $x$  can be represented as

$$x(\mathbf{r}, t) = x^+(\mathbf{r}, t)\Theta^+(f) + x^s(\mathbf{r}, t)\delta^s(\mathbf{r}, t) + x^-(\mathbf{r}, t)\Theta^-(f), \quad (1)$$

where the equation  $f(\mathbf{r}, t) = 0$  defines the phase interface,  $f(\mathbf{r}, t) > 0$  defines the region occupied by liquid, and  $f(\mathbf{r}, t) < 0$  defines the solid phase,  $\Theta^\pm(f)$  are Heaviside functions

$$\Theta^+(f) = \begin{cases} 1, & f > 0 \\ 0, & f \leq 0 \end{cases} \quad \Theta^-(f) = \begin{cases} 0, & f \geq 0 \\ 1, & f < 0, \end{cases}$$

$x^\pm$  are the densities of bulk variable  $x$  for each phase, which are labeled as + for the liquid and as – for the solid,  $x^s$  is the surface density. The surface  $\delta$ -function is defined as

$$\delta^s(\mathbf{r}, t) = |\nabla f| \delta(f(\mathbf{r}, t)),$$

where  $\delta(f)$  is the standard  $\delta$ -function.

Definition (1) means that the densities  $x$  become singular at the interface. Quantities  $x^s$  vary only along the surface but do not normally to the surface. Therefore, the normal derivatives of these quantities are zero.

In accordance to Eq. (1), the densities of internal energy  $u$ , entropy  $s$ , as well as the entropy production  $\sigma$  can be written in the form

$$u = u^+ \Theta^+ + u^s \delta^s + u^- \Theta^-, \quad (2)$$

$$s = s^+ \Theta^+ + s^s \delta^s + s^- \Theta^-, \quad (3)$$

$$\sigma = \sigma^+ \Theta^+ + \sigma^s \delta^s + \sigma^- \Theta^-, \quad (4)$$

where  $u^s$ ,  $\sigma^s$ , and  $s^s$  are the surface densities of these quantities and  $s^\pm$ ,  $\sigma^\pm$ , and  $u^\pm$  are their bulk densities. All quantities in Eqs. (2)–(4) are the functions of space–time point, however, the surface densities are defined only on the interface.

In a simplest approximation, we shall assume that the mass densities of both phases are constants. In addition, the dividing surface can be chosen in such a manner that one of excess densities may take zero value [17]. The mass density  $\varrho^s$  is usually chosen as such density. Also, we assume that the flow in phases is absent such that the velocity field becomes:

$$\mathbf{v} = \begin{cases} 0, & f > 0 \\ \mathbf{v}^s, & f = 0 \\ 0, & f < 0, \end{cases}$$

where  $\mathbf{v}^s$  is the velocity of the boundary (the front velocity) which is changing along the surface.

In the Gibbs model, the equilibrium surface temperature  $T^s$  is defined by the equality [17]

$$ds^s = \frac{1}{T^s} du^s \quad \text{with } \varrho^s = 0. \quad (5)$$

In equilibrium, one has  $T^s = T^+ = T^-$ , where  $T^\pm$  are the temperatures of bulk phases. In the absence of equilibrium, Eq. (5) defines the temperature of the surface element having the internal energy  $u^s$  and the entropy  $s^s$  [14]. Eq. (5) means that there is local equilibrium along surface.

As it has been noted in the introductory section, Onsager relations at the interface can be considered as boundary conditions. The derivation of these relations is based on the principle of positive definiteness of the entropy [11]. The detailed derivation for the surface entropy production  $\sigma^s$  for the solidification problem is provided in Appendix A and it gives

$$\sigma^s = -\mathbf{J}_q^s \left( \frac{1}{T^s} \right)^2 \nabla_{\parallel} T^s + \left[ \frac{\mu \varrho}{T} \right]_- v_n^s + [J_{qn} - h v_n^s]_+ \left( \frac{1}{T^+} - \frac{1}{T^-} \right) + [J_{qn} - h v_n^s]_- \left[ \frac{1}{2} \left( \frac{1}{T^+} + \frac{1}{T^-} \right) - \frac{1}{T^s} \right], \quad (6)$$

where  $\mathbf{J}_q^s$  is the surface density of the heat flux  $\mathbf{J}_q$  defined in consistency with Eq. (1). In what follows, all bulk quantities, entering in the equations at the interface [see, for example, Eq. (6)], present their limiting values  $x^\pm$  at the interface, and, for the jump of  $x$  through the interface, the following notations have been introduced

$$[x]_- = x^+ - x^-,$$

$$[x]_+ = \frac{1}{2}(x^+ + x^-).$$

Therefore, in Eq. (6),  $\mu$  is the chemical potential,  $\varrho$  is the mass density,  $h$  is the enthalpy and  $T^\pm$  are the boundary temperatures of phases. The heat flux in the normal direction to the interface is denoted as  $J_{qn}^\pm = \mathbf{n} \cdot \mathbf{J}_q^\pm$ , where  $\mathbf{n}$  is the unit vector to the interface and  $v_n^\pm = \mathbf{n} \cdot \mathbf{v}^\pm$  is the normal component of the interface velocity. The surface heat flux  $\mathbf{J}_q^s$  lies in the tangent plane and its scalar product with any vector along normal is zero. The symbol  $\parallel$  defines the component of a vector along the tangent plane to the interface.

### 3. Boundary conditions

Equality (6) can be represented as a sum of products of the dissipative fluxes and conjugated driving forces. Then, taking into account the positivity of entropy production,  $\sigma^s \geq 0$ , one can write down linear relations between this quantities. We take  $\nabla_{\parallel} T^s$ ,  $[\mu \varrho / T]_-$ ,  $[1/T]_-$ , and

$$\frac{1}{2} \left( \frac{1}{T^+} + \frac{1}{T^-} \right) - \frac{1}{T^s},$$

as the driving forces and  $\mathbf{J}_q^s$ ,  $v_n^s$ , and  $[J_{qn} - h v_n^s]_+$ ,  $[J_{qn} - h v_n^s]_-$  as the dissipative fluxes.

The selected driving forces are independent, because they describe different phenomena: (a) the heterogeneity in the surface temperature (surface temperature gradient); (b) the transformation of one phase to another (a jump of the chemical potential); (c) the lack of thermal equilibrium at the phase boundary (temperature jump); (d) the deviation of surface temperature from the temperatures of the bulk phases at the interface.

Thus, there are the vectorial force–flux pair and three scalar force–flux pairs in Eq. (6). Taking into account tensorial nature of the various quantities with their isotropy at the surface and in bulk, we have linear laws as

$$\mathbf{J}_q^s = -\lambda^s \nabla_{\parallel} T^s, \quad (7)$$

and

$$v_n^s = L_{00} \left[ \frac{\mu Q}{T} \right]_- + L_{01} \left( \frac{1}{T^+} - \frac{1}{T^-} \right) + L_{02} \left[ \frac{1}{2} \left( \frac{1}{T^+} + \frac{1}{T^-} \right) - \frac{1}{T^s} \right], \quad (8)$$

$$[J_{qn} - hv_n^s]_+ = L_{10} \left[ \frac{\mu Q}{T} \right]_- + L_{11} \left( \frac{1}{T^+} - \frac{1}{T^-} \right) + L_{12} \left[ \frac{1}{2} \left( \frac{1}{T^+} + \frac{1}{T^-} \right) - \frac{1}{T^s} \right], \quad (9)$$

$$[J_{qn} - hv_n^s]_- = L_{20} \left[ \frac{\mu Q}{T} \right]_- + L_{21} \left( \frac{1}{T^+} - \frac{1}{T^-} \right) + L_{22} \left[ \frac{1}{2} \left( \frac{1}{T^+} + \frac{1}{T^-} \right) - \frac{1}{T^s} \right], \quad (10)$$

where  $\lambda^s$  has a meaning of surface heat conductivity and  $L_{ij}$  are the kinetic coefficients satisfying the Onsager reciprocal conditions,  $L_{ij} = L_{ji}$ .

Expression (7) connects the surface heat flux  $\mathbf{J}_q^s$  with the temperature  $T^s$  analogously to the Fourier law for the bulk transport. Relations (8)–(10) give boundary conditions for the bulk quantities. Expression (8) defines the interface velocity. Equality (10) presents a difference between the energy fluxes on the both sides of the interface (energy flux jump) and Eq. (9) defines their half-sum. When the energy flux is continuous across the phase boundary, the left side of equality (9) is equal to the energy flux. As it follows from Eq. (8), thermodynamic conditions for crystallization (i.e., conditions of non-zero interface velocity) are determined by the difference of the chemical potentials, the temperature jump, and also by the difference of boundary temperatures in phases from the interface temperature  $T^s$ .

In addition, relations (8)–(10) should be completed for the interface temperature  $T^s$  (see Eq. (A.21))

$$c^s \frac{dT^s}{dt} + \text{div} \mathbf{J}_q^s + T^s s^s \text{div} \mathbf{v}^s = [hv_n^s - J_{qn}]_-, \quad (11)$$

where  $c^s$  is the interfacial heat capacity. The dissipation of an energy and its transfer along the interface give rise to the interface temperature changes and are taken into account in Eq. (11) by the energy flux jump in the right hand side of this equation and the surface heat flux  $\mathbf{J}_q^s$ . At the steady-state solidification (i.e., in the regime with the constant interface velocity along the interface) and for homogeneous interface ( $\mathbf{J}_q^s = 0$ ), the left hand side of Eq. (11) is equal to zero that leads to the conservation of the energy flux through the interface.

System of Eqs. (7)–(11) represents complete system of boundary conditions at the phase interface. After exclusion of the surface heat flux  $\mathbf{J}_q^s$  by the relation (7), these boundary conditions can be considered as the system of four equations with four unknown quantities: two boundary temperatures  $T^\pm$ , growth velocity  $v_n^s$  and interface temperature  $T^s$ . In what follows this system of equations are applied to the motion of planar solidification front with constant velocity.

#### 4. Steady-state interface motion

Consider the homogeneous interface which is moving with the constant velocity and the energy dissipation at the interface is absent. In this case Eq. (11) gives equality of energy fluxes at the both sides of interface:

$$[J_{qn} - hv_n^s]_- = 0. \quad (12)$$

Then, from Eq. (10) one gets the equality

$$L_{20} \left[ \frac{\mu Q}{T} \right]_- + L_{21} \left( \frac{1}{T^+} - \frac{1}{T^-} \right) + L_{22} \left[ \frac{1}{2} \left( \frac{1}{T^+} + \frac{1}{T^-} \right) - \frac{1}{T^s} \right] = 0,$$

which defines the surface temperature as

$$\frac{1}{T^s} = \frac{1}{2} \left( \frac{1}{T^+} + \frac{1}{T^-} \right) + \frac{L_{20}}{L_{22}} \left[ \frac{\mu Q}{T} \right]_- + \frac{L_{21}}{L_{22}} \left( \frac{1}{T^+} - \frac{1}{T^-} \right). \quad (13)$$

With the accuracy up to small thermodynamic forces,  $[\mu Q/T]_-$ ,  $[1/T]_-$ , Eq. (13) gives

$$\frac{1}{T^s} = \frac{1}{2} \left( \frac{1}{T^+} + \frac{1}{T^-} \right). \quad (14)$$

As it follows now from Eq. (8), the interface velocity is defined by two quantities:  $[\mu Q/T]_-$  and  $[1/T]_-$ . Because  $v_n^s$  must be zero at  $T^s = T^+ = T^- = T_M$ , then  $[\mu Q/T]_-$  should take zero value for the same conditions. In this case, one can write the following expansion

$$\left[ \frac{\mu Q}{T} \right]_- = \mathcal{A} \left( \frac{1}{T^s} - \frac{1}{T_M} \right) + \mathcal{B} \left( \frac{1}{T^+} - \frac{1}{T^-} \right) + \dots, \quad (15)$$

where  $\mathcal{A}$  are  $\mathcal{B}$  some constants. Substituting first two terms of Eq. (15) into Eqs. (8)–(10), taking into account Eq. (14), and re-denoting kinetic coefficients ( $L \rightarrow L'$ ), one gets

$$v_n^s = L'_{00} \left( \frac{1}{T^s} - \frac{1}{T_M} \right) + L'_{01} \left( \frac{1}{T^+} - \frac{1}{T^-} \right), \quad (16)$$

$$[J_{qn} - hv_n^s]_+ = L'_{10} \left( \frac{1}{T^s} - \frac{1}{T_M} \right) + L'_{11} \left( \frac{1}{T^+} - \frac{1}{T^-} \right), \quad (17)$$

$$[J_{qn}]_- = L^s v_n^s + c_p [T]_- v_n^s. \quad (18)$$

Due to equality (12), the left hand side of Eq. (17) defines the energy flux  $J_E$  through the phase interface. Note that the coefficients  $L'_{ij}$  do not already satisfy the reciprocal Onsager relations, i.e.  $L'_{ij} \neq L'_{ji}$ .

Eq. (18) presents modified boundary condition of Stefan and it can be obtained from the equality (12) rewritten as

$$J_{qn}^+ - J_{qn}^- = (h^+ - h^-)v_n^s, \quad (19)$$

where  $h^+ - h^- = h^+(T^+) - h^-(T^-)$ , and

$$\begin{aligned} h^\pm(T^\pm) &= h^\pm(T^s + T^\pm - T^s) \\ &\approx h^\pm(T^s) + \left(\frac{\partial h^\pm}{\partial T^\pm}\right)_{T^s} (T^\pm - T^s) + \dots \end{aligned} \quad (20)$$

The derivative of enthalpy with respect to temperature defines the heat capacity at the constant pressure. Taking for simplicity the heat capacities in both phases to be approximately identical,  $\left(\partial h^\pm / \partial T^\pm\right)_{T^s} = c_p$ , one gets

$$\begin{aligned} h^+ - h^- &= h^+(T^s) - h^-(T^s) + c_p(T^+ - T^-) \\ &= L^s + c_p(T^+ - T^-). \end{aligned} \quad (21)$$

Here  $L^s = h^+(T^s) - h^-(T^s)$  can be interpreted as latent heat of solidification. Finally, substitution of Eq. (21) into Eq. (19) gives Eq. (18).

At the end of this section, one has to note that, considering the interface velocity  $v_n^s$  as a flux allows us compare Eq. (16) with the expression for the front velocity obtained from kinetic equation (see Appendix B and Section 5).

## 5. The temperature jump

The obtained boundary conditions are not limited by a specific model of heat transport in the bulk system and have a general meaning. Using Eqs. (16)–(18), we now calculate the temperature jump  $\Delta T = T^+ - T^-$  at the phase interface and the front velocity in a framework of parabolic model of heat transport.

Let us consider now crystallization of undercooled liquid. Assume that the planar interface is moving with the constant velocity  $v_n^s = V$  in the direction of their normal being  $z$ -axis. In this case the temperature and the heat flux in the system volume satisfy the one-dimension diffusion equation

$$\frac{\partial T^\pm(zt)}{\partial t} = \kappa^\pm \frac{\partial^2 T^\pm(zt)}{\partial z^2} \quad (22)$$

$$\frac{\partial J_q^\pm(zt)}{\partial t} = \kappa^\pm \frac{\partial^2 J_q^\pm(zt)}{\partial z^2}, \quad (23)$$

where  $\kappa^\pm$  are the heat conductivities of the phases. Further we assume the heat diffusion in solid phase is absent. Then Eqs. (22)–(23) have solutions in a form of traveling waves. In the liquid region,  $Z = z - Vt > 0$ , one has

$$T^+(zt) = T_0 + A_1 e^{-VZ/\kappa^+}, \quad (24)$$

$$J_q^+(zt) = A_2 e^{-VZ/\kappa^+}, \quad (25)$$

and in the region of solid phase,  $Z < 0$ , one gets

$$T^-(zt) = A_3, \quad J_q^-(zt) = 0, \quad (26)$$

where  $T_0$  is the initial temperature of liquid and  $A_i$  are constants. Then, at the interface,  $Z = 0$ , one can get the following values of temperature and heat flux for both phases (further the bulk state quantities at the interface will be wrote without arguments  $zt$ )

$$T^+ = T_0 + A_1, \quad J_q^+ \equiv J_{qn}^+ = c_p V A_1, \quad (27)$$

where the equality  $A_2 = c_p V A_1$ , following from the energy conservation law,  $c_p \partial T / \partial t = -\partial J_q / \partial z$ , have been used and

$$T^- = A_3, \quad J_q^- \equiv J_{qn}^- = 0. \quad (28)$$

Thus, we have three the independent constants  $A_1$ ,  $A_3$  and  $V$  in Eqs. (24)–(26) which can be defined from three equations (16)–(18). To determinate these quantities let us rewrite Eqs. (16)–(18) at small values of the deviation<sup>1</sup>  $T^\pm - T_M$  using the

<sup>1</sup> Indeed, approximations (29) and (30) are valid due to  $(T^\pm - T_M)/T_M \ll 1$  [19]. For example, for pure Ag at undercooling  $T_M - T_0 \sim 200 - 500$  K, the difference  $T_M - T^\pm \sim T_M - T^s$  can vary by  $\sim 0, 16T_M - 0, 24T_M$  during solidification [20].

following approximations

$$\frac{1}{T^s} - \frac{1}{T_M} = \frac{1}{2} \left( \frac{1}{T^+} + \frac{1}{T^-} \right) - \frac{1}{T_M} \simeq \frac{1}{2T_M^2} (T^+ + T^- - 2T_M) \quad (29)$$

$$\frac{1}{T^+} - \frac{1}{T^-} \simeq \frac{1}{T_M^2} (T^- - T^+). \quad (30)$$

Further, taking into account Eq. (20), one can write

$$[h]_+ = \frac{1}{2}(h^+ + h^-) = \frac{1}{2}[h^+(T^s) + h^-(T^s)] + \frac{1}{2}c_p(T^+ + T^- - 2T^s) + \dots \simeq \frac{H^s}{2} + \mathcal{O}(\Delta T^2), \quad (31)$$

where  $H^s/2 = [h^+(T^s) + h^-(T^s)]/2$ .

As a result, instead of Eqs. (16)–(18), one finds

$$V = \frac{L_1}{2}(T^+ + T^- - 2T_M) + L_2(T^- - T^+), \quad (32)$$

$$J_E = [U_{qn}]_+ - \frac{1}{2}H^sV = \frac{L_3}{2}(T^+ + T^- - 2T_M) + L_4(T^- - T^+), \quad (33)$$

$$[U_{qn}]_- = L^sV + c_pV(T^+ - T^-), \quad (34)$$

where the following notations

$$L_1 = \frac{L'_{00}}{T_M^2}, \quad L_2 = \frac{L'_{01}}{T_M^2}, \quad L_3 = \frac{L'_{10}}{T_M^2}, \quad L_4 = \frac{L'_{11}}{T_M^2},$$

have been introduced. Note that the coefficient

$$R = L_4^{-1}$$

has a meaning of the Kapitza coefficient.

Expressions for the temperature jump and the boundary temperatures can now be obtained from Eqs. (27)–(28) and Eqs. (33)–(34) as

$$\Delta T = R \frac{Vh^- + L_3(T_0 + L^s/c_p - T_M)}{1 - R(L_3 - c_pV)/2}, \quad (35)$$

$$T^+ = T_0 + L^s/c_p + \Delta T, \quad (36)$$

$$T^- = T_0 + L^s/c_p, \quad (37)$$

where  $h^- = h^-(T^s)$ . To simplify further calculations let us assume approximately for the evaluation the enthalpy that

$$h^- = h^-(T^s) \approx c_pT^s. \quad (38)$$

Using Eqs. (36)–(37), one has for the interfacial temperature  $T^s$

$$T^s = \frac{2T^+T^-}{T^+ + T^-} = \frac{2(T_0 + L^s/c_p + \Delta T)(T_0 + L^s/c_p)}{2T_0 + 2L^s/c_p + \Delta T}. \quad (39)$$

With the accuracy of second order by  $\Delta T$ , this expression gives

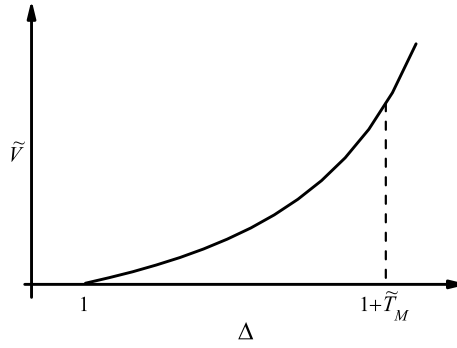
$$T^s = T_0 + \frac{L^s}{c_p} + \frac{\Delta T}{2} + \dots \quad (40)$$

Taking into account Eqs. (38) and (40), from Eq. (35) one obtains finally the expression for the temperature jump

$$\Delta T = \frac{Rc_pV(T_0 + L^s/c_p)}{1 - RL_3/2} \left\{ 1 - \frac{L_3}{c_pV} \left( \frac{T_M}{T_0 + L^s/c_p} - 1 \right) \right\}. \quad (41)$$

This expression generalizes the expression for the temperature jump found in Ref. [10] and reduces to it when  $L_3 = 0$ :

$$\Delta T = Rc_pV \left( T_0 + \frac{L^s}{c_p} \right). \quad (42)$$



**Fig. 1.** Dependence of dimensionless velocity  $\tilde{V}$  on undercooling  $\Delta$ ;  $a = \frac{1}{2}\tilde{R}(1 + 2L_2/|L_1|) > 0$ .

Together with Eqs. (36)–(37), Eq. (41) allows us to obtain equation for the interface velocity  $V$ . From the boundary condition (32) and Eqs. (36)–(37), one gets

$$V = -L_1 \left( T_M - T_0 - \frac{L^s}{c_p} \right) + \left( \frac{L_1}{2} - L_2 \right) \Delta T. \quad (43)$$

With the zero temperature jump,  $\Delta T = 0$ , one can obtain known expression for the interface velocity which is linearly dependent from undercooling,  $\theta = T_M - T_0 - L^s/c_p$ , with  $L_1 = L'_{00}/T_M^2 < 0$  having the meaning of the kinetic coefficient of crystal growth [see also Eq. (B.4)].

To simplify the further analysis, Eq. (42) for the temperature jump is used, i.e. it is assumed that  $L_3 = 0$ . Then substituting expression (42) into Eq. (43), one obtains for the interface velocity

$$V = \frac{|L_1|(T_M - T_0 - L^s/c_p)}{1 + Rc_p(|L_1|/2 + L_2)(T_0 + L^s/c_p)}. \quad (44)$$

Under the assumed approximations, Eqs. (36)–(37), (42) and (44) completely solve the problem of finding boundary temperatures and the interface velocity.

Relation (44) allows us to analyze the interface velocity depending on the initial undercooling of the liquid phase. With this aim we rewrite Eq. (44) in the dimensionless form

$$\tilde{V} = \frac{\Delta - 1}{1 - \frac{1}{2}\tilde{R}(1 + 2L_2/|L_1|)(\Delta - 1 - \tilde{T}_M)}, \quad (45)$$

where  $\tilde{V} = c_p V / L^s |L_1|$  is the dimensionless interface velocity,  $\tilde{R} = RL^s |L_1|$  is the dimensionless Kapitza resistance,  $\tilde{T}_M = c_p T_M / L^s$  and  $\Delta = (c_p / L^s)(T_M - T_0)$  is the dimensionless undercooling determining the deviation of the solidification temperature  $T_M$  from the temperature  $T_0$  of the liquid phase far from interface. Due to inequality  $\Delta - 1 - \tilde{T}_M = -(c_p / L^s)(T_0 + L^s / c_p) < 0$ , one gets  $\Delta < 1 + \tilde{T}_M$ .

Various regimes of steady interface motion can be analyzed by Eq. (45) depending on  $\Delta$  and the parameter

$$a = \frac{1}{2}\tilde{R}(1 + 2L_2/|L_1|) = \frac{1}{2}RL^s |L_1|(1 + 2L_2/|L_1|), \quad (46)$$

which is proportional to the Kapitza resistance  $R$  and depends on the ratio of the kinetic coefficients  $L_1$  and  $L_2$ , determining the contribution of the temperature jump  $\Delta T$  in the interface velocity described by Eq. (43). Because  $L_2 = L'_{01}/T_M^2 < 0$  [see Eq. (B.5)], the parameter  $a$  may have different signs. Qualitative behavior of  $\tilde{V}$  is illustrated in Figs. 1–3. Only branches of the curves having a physical meaning are shown at the figures. Depending on the value of the parameter  $a$  one can consider three different regimes.

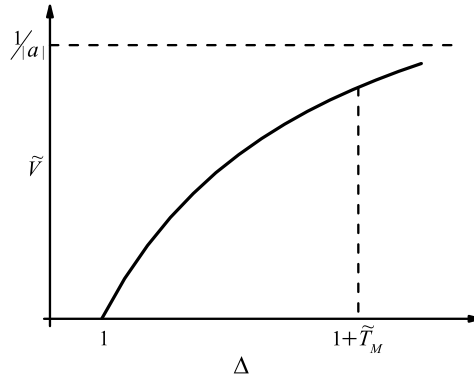
1. Fig. 1 presents the interface velocity for  $a > 0$  ( $|L_1| \gtrsim 2|L_2|$ ) within the range  $1 < \Delta < 1 + \tilde{T}_M$ . The maximal value of the velocity is reached at the right border and is equal to  $\tilde{V} = \tilde{T}_M$  (in the dimension form it is  $V_{max} = |L_1|T_M$ ).

2. Fig. 2 presents the interface velocity for  $a < 0$  ( $|L_1| < 2|L_2|$ ) and  $\tilde{T}_M + 1 - 1/|a| < 1$ . In the dimension form, the latter inequality is given by

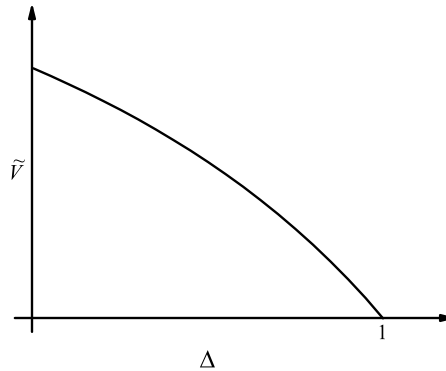
$$\frac{2}{c_p RT_M |2L_2 - L_1|} \sim \frac{2}{c_p RT_M |L_1|} > 1 \quad (L_2 \sim L_1). \quad (47)$$

This case corresponds to the small values of the Kapitza resistance. The velocity is defined within the range of undercooling  $1 < \Delta < \tilde{T}_M + 1$  and at  $L_2 \sim L_1$  its maximum is of the order of

$$V_{max} \sim \frac{1}{|a|} \sim \frac{2}{RL^s |L_1|}. \quad (48)$$



**Fig. 2.** Dependence of dimensionless velocity  $\tilde{V}$  on the undercooling  $\Delta$ ;  $a = \frac{1}{2}\tilde{R}(1 + 2L_2/|L_1|) < 0, \tilde{T}_M + 1 - 1/|a| < 1$ . Note that, at  $0 < \Delta < 1$ , the velocity is negative,  $\tilde{V} < 0$ .



**Fig. 3.** Dependence of dimensionless velocity  $\tilde{V}$  on undercooling  $\Delta$ ;  $a = \frac{1}{2}\tilde{R}(1 + 2L_2/|L_1|) < 0, \tilde{T}_M + 1 - 1/|a| > 1$ . Note that, at  $\Delta > 1$ , the velocity  $\tilde{V}$  has negative values or it reaches infinity.

3. Fig. 3 presents the interface velocity for  $a < 0$  and  $\tilde{T}_M + 1 - 1/|a| > 1$  or in the dimensional form

$$\frac{2}{c_p R T_M |L_1|} < 1 \quad (L_2 \sim L_1). \tag{49}$$

Inequality (49) corresponds to the large values of Kapitza resistance.

As it follows from Fig. 3, the velocity is defined within the undercooling range:  $0 < \Delta < 1$ . Due to  $\Delta < 1$  and Eq. (37), the temperature at the solid side of the interface becomes larger than the equilibrium melting point:  $T^- = T_0 + L^s/c_p > T_M$  (the overheated boundary layer of solid phase) but the crystallization front moves into the liquid,  $V > 0$ , as it is shown in Fig. 3. Such effect of heat trapping has been described in Refs. [5,21]. With the decrease of  $T_0$ , the temperature of the solid phase near the interface may reach the value  $T_M$  ( $\Delta = 1$ ) with  $V = 0$ . In this case the temperature at liquid side of the interface is also equal to the melting point  $T_M$  [see Eqs. (36) and (42)].

It should be noted that the behavior of the velocity near the value  $\Delta = 0$  in Fig. 3 is not physically realized because of the finiteness of the velocity at this point. However the movement of the front with the velocity determined by the curve near the right border, i.e. close to  $\Delta = 1$ , can take place. The steady state regime of crystal growth in the range  $1 - \Delta \ll 1$  and  $\Delta < 1$  has been found in previous works [22,23]. However, in these works, Kapitza resistance was not taken into account. We will return to this issue in next section.

As it is seen, Figs. 1–3 show nonlinear behavior of the velocity against undercooling. This non-linearity appears due to the heat Kapitza resistance. At  $R = 0$ , Eq. (45) exhibits linear dependence  $\tilde{V} = \Delta - 1$ . It is worth noting that the same linear dependency will occur when  $|L_1| = 2|L_2|$ . As it follows from Eq. (43), in this case, the temperature jump  $\Delta T$  does not affect the interface velocity.

### 6. Concluding remarks

In the present work boundary conditions at the solidification front taking into account the temperature discontinuity at the interface have been obtained. The interface was considered in the framework of Gibbs model of the dividing surface for which the surface thermodynamical variables, such as the temperature, the entropy, the energy, the flux densities and



so on, have been introduced independently of the corresponding bulk quantities. Boundary conditions (7)–(10) represent the Onsager relations at the interface and together with Eq. (11) for the interface temperature make up the complete set of equations for finding the boundary temperatures of the bulk phases  $T^\pm$ , the interface temperature  $T^s$  and the solid growth velocity  $v_n^s$ . Eq. (11) describes change of the interface temperature due to energy dissipation at the interface.

The boundary conditions (7)–(10) have been applied to the analysis of the steady state regime of the planar interface motion. In the absence of the energy dissipation at the interface and for states close to equilibrium we have derived the expression for the temperature jump at the interface generalizing the previous result of Ref. [10]. The obtained expression, Eq. (41), is proportional to the Kapitza resistance  $R$  (see Ref. [10]) and it also includes the additional kinetic coefficient  $L_3$  taking into account dependence of the interfacial energy flux from the deviation of the interface temperature  $T^s$  from equilibrium melting temperature  $T_M$  (see Eq. (33)).

Using boundary conditions (32)–(34), possible steady state regimes of the crystallization front have been analyzed depending from the undercooling of liquid  $\Delta$  and heat resistance of Kapitza  $R$ . Various cases are presented in Figs. 1–3 for  $L_3 = 0$ . At  $\Delta > 1$ , the steady state motion of planar front is possible for two cases:

- (a) if  $|L_1| > 2|L_2|$ , where  $L_1$  is the kinetic coefficient of solid growth and  $L_2$  is the kinetic coefficient which defines dependence of front velocity from temperature jump  $\Delta T$  [see Eq. (32)]. In this case the maximal interface velocity is equal to  $V_{\max} = |L_1|T_M$ ;
- (b) if  $|L_1| < 2|L_2|$  and at relatively small Kapitza resistance  $R$ , defined by inequality (47). The maximal interface velocity is given by Eq. (48),  $V_{\max} \sim 2/RL^2|L_1|$ .

Figs. 1 and 2 present “velocity-undercooling” relationship which are qualitatively coincide with the experimentally obtained relationships for some solidifying pure metals [20,24–27]. It should be noted that depending on the material, the experimental curves show the curvature of different signs similar to the curves in Figs. 1 and 2. Within the results of the present work, different curvatures and slopes of the “velocity-undercooling” relationship appear due to specific features of the solid–liquid interface having different microstructure at every of specific metal. As it follows from the results of the presented work, the curvature of the kinetic curves, Figs. 1 and 2, is determined through the ratio between the kinetic coefficients  $L_1$  and  $L_2$ .

For large enough values of Kapitza resistance  $R$  given by the inequality (49), the steady state regime of crystallization is also possible at  $\Delta < 1$  in a region  $1 - \Delta \ll 1$  (see Fig. 3). In such case, the interface moves with the overheated boundary layer of solid phase, when its temperature  $T^-$  is above the equilibrium melting temperature  $T_M$ ,  $T^- > T_M$ . The effect has been predicted in Refs. [21–23] on the basis of phase field method. It should be noted that the stability of this regime should be specially tested (see results and discussions in Refs. [22,23]). Here we just mention that Fig. 3 represents the anomalous crystal growth regime in which the solid–liquid interface velocity decreases with the increase of undercooling. Indeed, according to the outcomes of the thermodynamics of irreversible processes [11], the reaction of the system (the interface velocity,  $V$ ) should be increased with the increase of the driving force (the undercooling,  $\Delta$ ) that is in contradiction with the curve of Fig. 3. However, large values of the Kapitza resistance lead namely to such anomalous regime. Qualitatively the same anomalous regime shown in Fig. 3 has been observed in solidification of undercooled AlNi alloy melts [28].

Finally, let us make one essential remark. The whole analysis has been done for the constant Kapitza resistance  $R$  independent from temperature. However, measurements made at low and high temperatures [29,30] show that the heat resistance increases by the power law with decreasing temperature. In solidification experiments, therefore, the dependence of Kapitza coefficient from the melt initial temperature or undercooling is possible that can be qualitatively expressed, for example, as

$$R = R_0 + R_1 \Delta^\beta \quad (\beta > 0),$$

with positive constant  $R_0$  and  $R_1$ . At  $R_1 \ll R_0$ , the Kapitza resistance is almost independent from the temperature,  $R \approx R_0$ . In this case, depending on the relation between the kinetic coefficients, the interface velocity will behave analogously to the curves shown in Figs. 1 and 2.

In the liquid phase with  $R_1 \gtrsim R_0$ , the heat resistance  $R$  may take high enough values at  $\Delta \sim 1$ ,  $R \sim R_0 + R_1$ , for which the steady state regime can be realized analogously to the regime shown in Fig. 3 closely to  $\Delta = 1$ . If such regime is realized, then, it can be detected indirectly. As it can be seen in Fig. 3, the front velocity decreases with the increase of undercooling  $\Delta$ . Quite possible, due to the large heat resistance at high undercooling, the solidification rate slows down as it was been observed in experiments [20,26,27].

## Acknowledgments

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## Appendix A. The entropy production

In this Appendix, the method of Bedeaux, Albano and Mazur (BAM-method) is applied to the problem of pure liquid solidification. Details of mathematical formalism are given in Refs. [14,15] (see also Ref. [18]).

To derive entropy production  $\sigma^s$  we use conservation laws in the following form [11]:

$$\frac{\partial \varrho \mathbf{v}}{\partial t} = -\operatorname{div} \mathbf{P}, \quad (\text{A.1})$$

$$\frac{\partial e}{\partial t} = -\operatorname{div} \mathbf{J}_e, \quad (\text{A.2})$$

$$\frac{\partial s}{\partial t} = -\operatorname{div}(s\mathbf{v} + \mathbf{J}_s) + \sigma, \quad (\text{A.3})$$

where  $\varrho$ ,  $e$  and  $s$  are the densities of mass, energy and entropy, respectively, given by Eq. (1). Analogously to Eq. (1), one can write the stress tensor  $\mathbf{P}$  and energy flux  $\mathbf{J}_e = \mathbf{P} \cdot \mathbf{v} + e\mathbf{v} + \mathbf{J}_q$ , where  $\mathbf{J}_q$  is the heat flux and  $\mathbf{J}_s$  is the entropy flux.

To obtain equations for densities  $x^\pm$  and  $x^s$ , the quantities of the form Eq. (1) are substituted in Eqs. (A.1)–(A.3) and the following relations are used [14]:

$$\frac{\partial \Theta^\pm}{\partial t} = \mp v_n^s \delta^s(\mathbf{r}, t)$$

$$\nabla \Theta^\pm = \pm \mathbf{n} \delta^s(\mathbf{r}, t)$$

$$\frac{d^s}{dt} \delta^s \equiv \left( \frac{\partial}{\partial t} + \mathbf{v}^s \cdot \nabla \right) \delta^s = 0,$$

where  $d^s/dt$  is the total derivative at the interface,  $v_n^s = \mathbf{n} \cdot \mathbf{v}^s$  is the normal components of the vector  $\mathbf{v}^s$  and  $\mathbf{n}$  is the unit normal vector to the interface directed to the liquid. After substitution, the coefficients of  $\Theta^+$ ,  $\Theta^-$  and  $\delta^s$  in each equation vanish separately [14]. If the term of the form of  $\mathbf{A} \cdot \nabla \delta^s$  appears then the normal component of the vector  $\mathbf{A}$  also must vanish,  $A_n = \mathbf{n} \cdot \mathbf{A} = 0$ .

As a result, Eq. (A.1) gives (with  $\varrho \mathbf{v} = 0$ ):

$$\Theta^+ \operatorname{div} \cdot \mathbf{P}^+ + \Theta^- \operatorname{div} \cdot \mathbf{P}^- + [\mathbf{n} \cdot (\mathbf{P}^+ - \mathbf{P}^-) + \operatorname{div} \cdot \mathbf{P}^s] \delta^s + \nabla \delta^s \cdot \mathbf{P}^s = 0. \quad (\text{A.4})$$

From this it follows

$$\operatorname{div} \cdot \mathbf{P}^\pm = 0, \quad (\text{A.5})$$

$$\operatorname{div} \cdot \mathbf{P}^s + \mathbf{n} \cdot (\mathbf{P}^+ - \mathbf{P}^-) = 0, \quad (\text{A.6})$$

$$\mathbf{n} \cdot \mathbf{P}^s = 0. \quad (\text{A.7})$$

Eq. (A.5) is the usual equation of equilibrium in each phase and expressions (A.6) and (A.7) represent boundary conditions at the interface. In Eq. (A.6),  $\mathbf{P}^\pm$  are taken at the surface (due to surface  $\delta$ -function in Eq. (A.4)), i.e., are the limiting values of the stress tensor at corresponding side of the interface. It what follows, if the bulk quantities  $x^\pm$  occur in equations related to the surface (in a manner of Eq. (A.4)), their limiting values at the surface are implied.

The similar treatment of Eq. (A.2) gives for the surface density  $e^s$ :

$$\frac{\partial e^s}{\partial t} = -\operatorname{div} \cdot (\mathbf{P}^s \cdot \mathbf{v}^s + e^s \mathbf{v}^s + \mathbf{J}_q^s) + [e v_n^s - J_{qn}]_-, \quad (\text{A.8})$$

$$J_{qn}^s = \mathbf{n} \cdot \mathbf{J}_q^s = 0, \quad (\text{A.9})$$

where for every bulk quantity  $x^\pm$  taken at the interface we introduce the notations

$$[x]_- = x^+ - x^-$$

and  $J_{qn}^\pm = \mathbf{n} \cdot \mathbf{J}_q^\pm$ . From Eq. (A.9) follows that the interface heat flux is directed only along the surface.

Since  $\varrho^s = 0$ , the total interfacial energy  $e^s$  is equal to the internal energy  $u^s$

$$e^s = u^s + \frac{1}{2} \varrho^s (v^s)^2 = u^s.$$

Therefore Eq. (A.8) also presents the equation for  $u^s$ . The equation for total derivative of  $u^s$  follows from Eq. (A.8)

$$\frac{d^s u^s}{dt} = -\operatorname{div}(\mathbf{P}^s \cdot \mathbf{v}^s + \mathbf{J}_q^s) - e^s \operatorname{div} \mathbf{v}^s + [e v_n^s - J_{qn}]_-. \quad (\text{A.10})$$

The equations in the bulk give usual the energy conservation laws in continuum medium.

Using the similar method, equation for the entropy balance gives for the entropy density  $s^s$  at the interface

$$\frac{d^s s^s}{dt} = -\operatorname{div} \mathbf{J}_s^s - s^s \operatorname{div} \mathbf{v}^s + [s v_n^s - J_{sn}]_- + \sigma^s,$$

$$J_{sn}^s = \mathbf{n} \cdot \mathbf{J}_s^s = 0, \quad (\text{A.11})$$

where  $\mathbf{J}_s^s$  is the surface entropy flux and  $J_{sn}^\pm = \mathbf{n} \cdot \mathbf{J}_s^\pm$  is the normal projection of the entropy flux  $\mathbf{J}_s^\pm$  from the bulk phases such that  $\mathbf{J}_s^\pm = \mathbf{J}_q^\pm / T^\pm$  [11].

Taking into account the equality (5), we assume now that the following equality is fulfilled on the moving surface,

$$\frac{d^s s^s}{dt} = \frac{1}{T^s} \frac{d^s u^s}{dt}. \quad (\text{A.12})$$

After substituting Eq. (A.10) into Eq. (A.12), one gets

$$\frac{d^s s^s}{dt} = -\text{div} \frac{\mathbf{J}_q^s}{T^s} + \mathbf{J}_q^s \cdot \nabla \frac{1}{T^s} - \frac{1}{T^s} \mathbf{\Pi}^s : \nabla \mathbf{v}^s - \frac{p^s}{T^s} \text{div} \mathbf{v}^s - \frac{1}{T^s} e^s \text{div} \mathbf{v}^s + \frac{1}{T^s} [\mathbf{n} \cdot \mathbf{P} \cdot \mathbf{v}^s + e v_n^s - J_{qn}]_-. \quad (\text{A.13})$$

Here the stress tensor  $\mathbf{P}^s$  is divided into the viscous part  $\mathbf{\Pi}^s$  and elastic part  $p^s$ , such that  $\mathbf{P}^s = \mathbf{\Pi}^s + p^s(1 - \mathbf{nn})$ , where  $p^s$  has the meaning of surface tension (with the accuracy to the sign) [14]. We also assume that the medium is isotropic and  $(1 - \mathbf{nn})$  is the tensor with the following components  $\delta_{\alpha\beta} - n_\alpha n_\beta$ , and  $n_\alpha$  is the projections of the vector  $\mathbf{n}$ . The tensor  $(1 - \mathbf{nn})$  projects vectorial and tensorial quantities to the tangent plane to the interface and provides the condition  $\mathbf{\Pi}^s \cdot \mathbf{n} = 0$  which is follow from Eq. (A.7).

After some algebra, comparison of Eq. (A.13) with Eq. (A.11) gives

$$\mathbf{J}_s^s = \frac{\mathbf{J}_q^s}{T^s} \quad (\text{A.14})$$

$$\begin{aligned} \sigma^s = & -\frac{1}{T^s} \mathbf{\Pi}^s : \nabla \mathbf{v}^s - \mathbf{J}_q^s \cdot \left( \frac{1}{T^s} \right)^2 \nabla T^s + \frac{1}{T^s} [(\mathbf{n} \cdot \mathbf{\Pi})_{\parallel}]_- \cdot \mathbf{v}_{\parallel}^s - \frac{\pi^s}{T^s} \text{div} \mathbf{v}^s + \frac{1}{T^s} [\mu_Q + \Pi_{nn}]_- v_n^s \\ & + [J_{qn} - sT v_n^s]_+ \left( \frac{1}{T^+} - \frac{1}{T^-} \right) + [J_{qn} - sT v_n^s]_- \left[ \frac{1}{2} \left( \frac{1}{T^+} + \frac{1}{T^-} \right) - \frac{1}{T^s} \right], \end{aligned} \quad (\text{A.15})$$

here  $[x]_{\pm} = \frac{1}{2}(x^+ + x^-)$  for  $x^\pm$  at the interface,  $\mathbf{\Pi}^\pm = \mathbf{P}^\pm - p^\pm 1$  defines the viscous part of stress tensor  $\mathbf{P}^\pm$  with  $p^\pm$  being the hydrostatic pressure, and

$$\begin{aligned} \overset{\circ}{\mathbf{\Pi}}^s &= \mathbf{\Pi}^s - \pi^s(1 - \mathbf{nn}) \\ \pi^s &= \frac{1}{2} \text{Sp} \mathbf{\Pi}^s \\ (\mathbf{n} \cdot \mathbf{\Pi})_{\parallel} &= (1 - \mathbf{nn}) \cdot (\mathbf{n} \cdot \mathbf{\Pi}) \\ \Pi_{nn} &= \mathbf{n} \cdot \mathbf{\Pi} \cdot \mathbf{n}, \end{aligned}$$

where  $v_{\parallel}^s$  is the component of  $\mathbf{v}^s$  tangent to the interface and  $\mu^\pm$  are chemical potentials in bulk phases. In the derivation of Eq. (A.15) we used the relations

$$\mu^\pm \varrho^\pm = e^\pm - T^\pm s^\pm + p^\pm \quad (\text{A.16})$$

for the bulk quantities [11] and

$$e^s = T^s s^s - p^s \quad (\text{A.17})$$

for the surface energy density with  $\varrho^s = 0$  [14].

Relations (A.15) define the surface entropy production taking into account the heat transfer along the interface as well as effects of the surface and the bulk viscosities (see terms in Eq. (A.15) containing viscous stress tensors  $\overset{\circ}{\mathbf{\Pi}}^s$ ,  $\pi^s$ ,  $\mathbf{\Pi}^\pm$ ). The relation (A.15) is greatly simplified if we neglect the surface viscosity and take into account that in the stagnant medium,  $\mathbf{\Pi}^\pm = 0$ . In such case the interfacial entropy production takes the following form

$$\sigma^s = -\mathbf{J}_q^s \cdot \left( \frac{1}{T^s} \right)^2 \nabla T^s + \frac{1}{T^s} [\mu_Q]_- v_n^s + [J_{qn} - sT v_n^s]_+ \left( \frac{1}{T^+} - \frac{1}{T^-} \right) + [J_{qn} - sT v_n^s]_- \left[ \frac{1}{2} \left( \frac{1}{T^+} + \frac{1}{T^-} \right) - \frac{1}{T^s} \right]. \quad (\text{A.18})$$

Introducing now the bulk transverse flux of energy,  $J_E = J_{qn} - (sT + \mu_Q)v_n^s = J_{qn} - h v_n^s$ , where  $h = sT + \mu_Q = e + p$  is the enthalpy, the entropy production Eq. (A.18) can be finally rewritten as

$$\sigma^s = -\mathbf{J}_q^s \cdot \left( \frac{1}{T^s} \right)^2 \nabla_{\parallel} T^s + \left[ \frac{\mu_Q}{T} \right]_- v_n^s + [J_{qn} - h v_n^s]_+ \left( \frac{1}{T^+} - \frac{1}{T^-} \right) + [J_{qn} - h v_n^s]_- \left[ \frac{1}{2} \left( \frac{1}{T^+} + \frac{1}{T^-} \right) - \frac{1}{T^s} \right]. \quad (\text{A.19})$$

In obtaining Eq. (A.19), there was taken into account that the surface heat flux lies in the tangent plane and it has zero scalar product with any vector being normal to the surface. The symbol  $\parallel$  means the component of a vector along tangent plane and  $\nabla_{\parallel} = (1 - \mathbf{nn}) \cdot \nabla$ .

Equality (A.19) should be added by the equation for the interfacial temperature which can be derived from the equation for the interfacial internal energy (A.10). Assuming that  $u^s = u^s(T^s)$ ,

$$\frac{d^s u^s}{dt} = c^s \frac{d^s T^s}{dt},$$

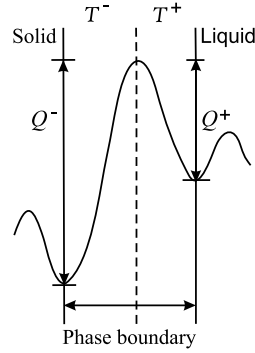


Fig. B.4. The atomic potential profile through the phase boundary with the temperature jump  $T^+ - T^-$ .

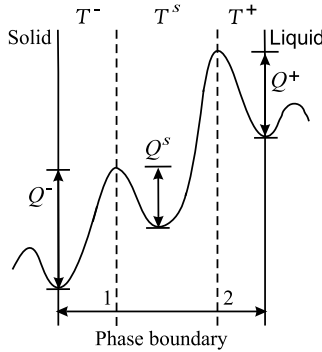


Fig. B.5. The atomic potential profile through the phase boundary, that is considered as a thermodynamic system with its own temperature  $T^s$ .

where  $c^s$  is the heat capacity of the interface, and using equalities (A.16) and  $\mathbf{P}^s = \mathbf{\Pi}^s + p^s(1 - \mathbf{nn})$ , one obtains from Eq. (A.10) the following equation for interfacial temperature:

$$c^s \frac{dT^s}{dt} = -\text{div} \mathbf{J}_q^s - \mathbf{\Pi}^s : \nabla \mathbf{v}^s + [\mathbf{n} \cdot \mathbf{\Pi} \cdot \mathbf{v}^s]_- T^s s^s \text{div} \mathbf{v}^s + [h\nu_n^s - J_{qn}]_- \quad (\text{A.20})$$

Neglecting the viscosity, one obtains finally

$$c^s \frac{dT^s}{dt} + \text{div} \mathbf{J}_q^s + T^s s^s \text{div} \mathbf{v}^s = [h\nu_n^s - J_{qn}]_- \quad (\text{A.21})$$

## Appendix B. Interface kinetics

In the absence of local equilibrium at the solidification front the usual kinetic equation for the rate of phase transformations [31] must be modified to take into account for the temperature discontinuity across the interface. In this section we consider a possible modification that is appropriate for the model of Gibbs, when the interface has its own temperature different from the boundary temperature of the bulk phases.

During crystallization the atoms must overcome an energy barrier separating different phases. Energy spatial distribution, shown in Fig. B.4 in which  $Q^\pm$  are the heights of energy barriers, is used for both continuous and discontinuous changes of temperature across the interface [6,31]. If the surface phase is characterized by the temperature  $T^s$  (which is different from the temperature  $T^+$  and  $T^-$  from sides of the interface), one can suppose to use energy profile as depicted in Fig. B.5. Atoms which overcome the barrier between liquid and surface layer 2 at the temperature  $T^+$  should also overcome the barrier  $Q^s$  between surface 1 and solid phase at the temperature  $T^s$ .

Thus, the process of transition of particles from the liquid phase in the solid can be described as follows. If  $j^+ = A_2 e^{-Q^+/kT^+}$  (with  $k$  being Boltzmann's constant) is the flux for the atomic attachment to the boundary 1, then only a part of this flux,  $A_3 j^+ e^{-Q^s/kT^s}$ , may reach the solid phase. The atomic detachment flux from the solid phase is given by  $j^- = B e^{-Q^-/kT^-}$ . For simplicity, we assume that the return flux from the interface into the liquid phase (through boundary 2) is negligible, i.e. the energy barrier in this direction is large enough. In this case, the rate of the growth of the new phase should mainly be

determined by kinetics on the boundary 1. Then, the flux difference at the boundary 1 gives the equation for the growth velocity

$$v^s = Ae^{-Q^+/kT^+} e^{-Q^s/kT^s} - Be^{-Q^-/kT^-}, \quad (\text{B.1})$$

where  $A = A_2A_s$  and  $B$  are positive constants having the dimension of velocity. In equilibrium, one has  $v^s = 0$  at the melting temperature  $T_M$  that allows us to write down Eq. (B.1) as

$$v^s = Ae^{-Q^+/kT^+ - Q^s/kT^s} \left\{ 1 - \exp \left[ \frac{[Q]_- + Q^s}{k} \left( \frac{1}{T^s} - \frac{1}{T_M} \right) \right] \exp \left[ \frac{[Q]_+}{k} \left( \frac{1}{T^+} - \frac{1}{T^-} \right) \right] \right. \\ \left. \times \exp \left[ -\frac{[Q]_-}{2k} \left( \frac{2}{T^s} - \frac{1}{T^+} - \frac{1}{T^-} \right) \right] \right\}, \quad (\text{B.2})$$

where  $[Q]_- = Q^+ - Q^-$ ,  $[Q]_+ = \frac{1}{2}(Q^+ + Q^-)$ .

Due to Eq. (13),

$$\frac{1}{T^s} = \frac{1}{2} \left( \frac{1}{T^+} + \frac{1}{T^-} \right),$$

one can get from Eq. (B.2)

$$v^s = Ae^{-Q^+/kT^+} \exp \left[ -\frac{Q^s}{2k} \left( \frac{1}{T^+} + \frac{1}{T^-} \right) \right] \left\{ 1 - \exp \left[ \frac{[Q]_+}{k} \left( \frac{1}{T^+} - \frac{1}{T^-} \right) \right] \right. \\ \left. \times \exp \left[ \frac{[Q]_- + Q^s}{2k} \left( \frac{1}{T^+} + \frac{1}{T^-} - \frac{2}{T_M} \right) \right] \right\}. \quad (\text{B.3})$$

It is easy to show that when the temperature continuously changes across the interface,  $T^+ = T^-$ , and there is no internal energy barrier,  $Q^s = 0$ , Eq. (B.3) is reduced to the known expression for the solidification rate of a pure liquid with  $Q^- - Q^+$  being latent heat solidification [31]. In the case of the temperature discontinuity at the phase boundary,  $T^+ \neq T^-$ , and at  $Q^s = 0$ , Eq. (B.3) coincides with the kinetic equation used in the work [6].

The equality (B.3) allows us to obtain kinetic coefficients  $L'_{00}$  and  $L'_{01}$  from Eq. (15) by the energy parameters. Indeed, expanding Eq. (B.3) in powers  $1/T^s - 1/T_M$  and  $1/T^+ - 1/T^-$ , and comparing the result with Eq. (15), one obtains for the kinetic coefficients

$$L'_{00} = -\frac{A}{k} (Q^s + [Q]_-) e^{-(Q^+ + Q^s)/kT_M}, \quad (\text{B.4})$$

$$L'_{01} = -\frac{A}{k} [Q]_+ e^{-(Q^+ + Q^s)/kT_M} < 0. \quad (\text{B.5})$$

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